

Introduction to carbon dioxide sequestration—based cementitious construction materials

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1.1 The cause for carbon dioxide sequestration

Data from ice cores show that in the last 400,000 years carbon dioxide (CO₂) varied with global temperature. Fig. 1.1 shows that for thousands of years the concentration level of atmospheric CO₂ has never risen above 300 per million (ppm). In the early 18th century, in the beginning of the Industrial Revolution, CO₂ was 280 ppm but since then it had risen in a steadily manner. And as a consequence 2016 was the first year with atmospheric CO₂ concentrations above 400 ppm all year round (Bets et al., 2016). Stern (2006) predicted that by 2050 CO₂ concentrations will rise above 550 ppm. And some doomsday scenarios even mention that keeping the current level of emissions will imply a dramatic increase in CO₂ concentration to as much as

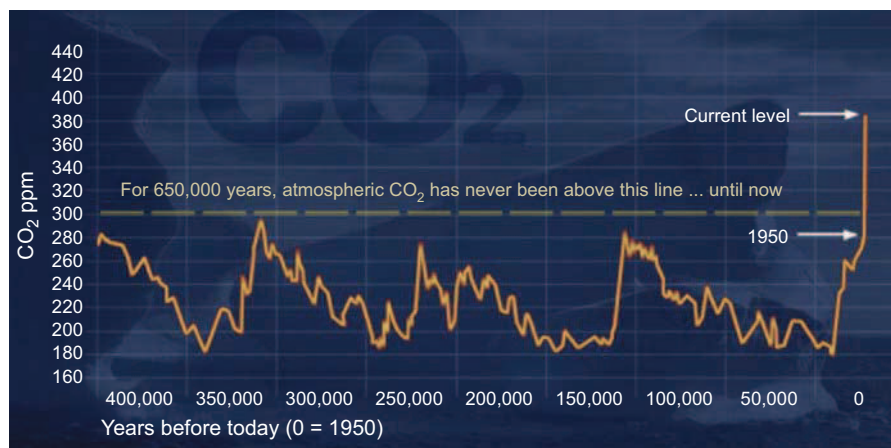


Figure 1.1 CO₂ (ppm) trend over years.

Based on data from NASA Vijayavenkataraman, S., Iniyan, S., Goic, R., 2012. A review of climate change, mitigation and adaptation. *Renewable and Sustainable Energy Reviews* 16 (1), 878–897. Copyright © 2012, with permission from Elsevier.

731 ppm in the year 2130, leading to a 3.7°C global warming above preindustrial temperatures (Valero et al., 2011). Recent studies show that even higher temperatures are expected (Hand, 2017).

The fact that CO₂ concentrations had reached 400 ppm means that the 350 ppm boundary set in the global sustainability model by Rockstrom et al. (2009) was already crossed risking “*abrupt environmental change within continental-to planetary-scale systems*”. Global warming can trigger the thawing of the permafrost—permanently frozen ground—(Schadel et al., 2016; Voigt et al., 2016; Wilson et al., 2017), where approx. 1×10^6 million tons (1000 GtCO₂eq) are still retained, and this can dramatically change global warming side effects. This astonishing figure is equivalent to the current worldwide production (34 GtCO₂eq) during 30 years. Hansen et al. (2013) believes that the climate has already been changed in an irreversible manner. The Union of Concerned scientists (Ripple et al., 2017) also find especially troubling the current trajectory of potentially catastrophic climate change due to rising greenhouse gas emissions from burning fossil fuels. A worrying sign that justifies Hansen’s view comes from a recent study (McMillan et al., 2014) based on the measurements collected by the Cryosat-2 satellite, which reported an annual loss of 159,000 million tons of the Antarctic ice sheet. This represents a 200% ice loss rate when compared with the 2005–10 previous survey. Recent satellite observations show that one of the largest icebergs ever recorded (Larsen C), twice the size of the Luxembourg and with up to 350 m thick, is on the verge to be released (Sumner, 2017). This eminent collapse will have a direct impact on sea level rise. Although global sea levels are rising by about 3 mm a year, the glaciers that flow into Larsen C contain enough water to raise the global sea level by about a centimeter (Tollefson, 2017). And in fact the Larsen C collapsed on July of 2017 and all we have to do now is to watch for the consequences of that event. It is worth mentioning that 10 years ago IPCC (2007) already predicted that when the sea level rises above 0.40 m, it will submerge 11% of the area of Bangladesh leading to almost 10 million homeless. Increasing atmospheric CO₂ levels will also lead to ocean acidification (Hofmann and Schellnhuber, 2010; Harrould-Kolieb and Herr, 2012; Perez et al., 2018; Mollica et al., 2018). This changes sea water chemical speciation, lowering calcium carbonate saturation states, thus damaging coral reefs (Frieler et al., 2013; Allen et al., 2016; Altieri et al., 2017) and putting habitats of high economic value at risk. It is worth remembering that coral reef habitats represent fish resources that are important to develop countries (Cooley and Downey, 2009) and that they also feed more than 1000 million people (Bourne, 2008; Anthony et al., 2008) and have an economic value estimated at 97–300 billion dollars/year (Colt and Knapp, 2016). It is important to mention also the probable meltdown of the world economy associated with climate change. According to Stern (2006), if we act now, the cost of all the services and products to tackle climate change will be 1% of the gross domestic product (GDP), otherwise, an economic depression of about 20% GDP may take place. Some authors (Parham et al., 2015) argue that one of the most important effects of climate change is the potential impact on human health. A warming atmosphere increases vector-borne diseases (VBD), which rely upon organisms, named vectors, such as mosquitoes (*Aedes aegypti*, *Aedes albopictus*, *Aedes japonicus*) and other insects, that have an active role in the transmission of a pathogen, have been

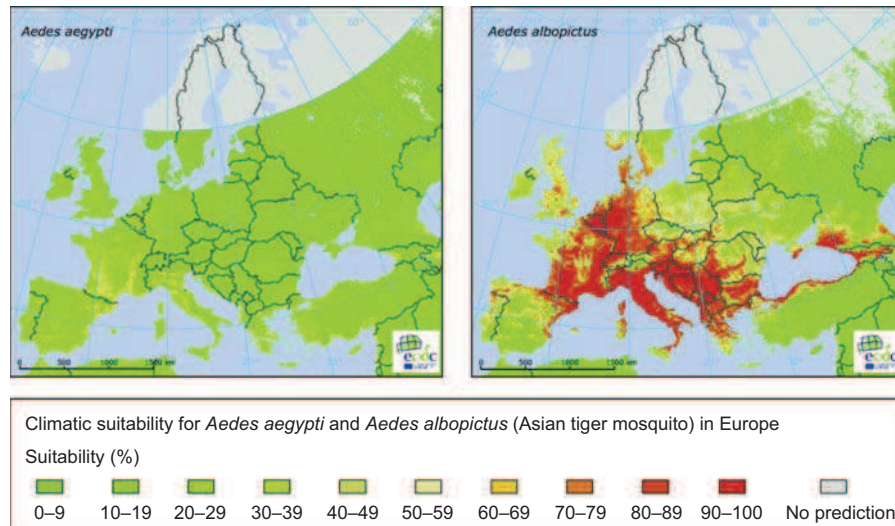


Figure 1.2 Climatic suitability for the Asian tiger mosquito in Europe (EEA, 2016).

projected to increase both in geographic reach as well as severity (McMichael et al., 2006; IPCC, 2012; Caminade et al., 2016; Ogden and Lindsay, 2016). Also, the European Environmental Agency presents a dreadful projection for VBD. Fig. 1.2 shows the climatic suitability for the Asian tiger mosquito (*A. albopictus*), which is known to disseminate several diseases such as the Zika virus responsible for birth defects such as microcephaly (EEA, 2016).

A much worrying public health problem is related to the fact that climate change is bringing back to life deadly viruses and bacteria that lay dormant for hundreds and even thousands of years. In 2016 it was reported that a 12-year-old boy died and at least 20 individuals hospitalized due to an anthrax outbreak in the Yamal peninsula near the Arctic. The infection came from the carcasses of infected reindeer frozen in the permafrost for 75 years that the heat wave of 2016 had thawed (Fox-Skelley, 2017). Climate change is also responsible for shifting weather patterns, threatening food production through increased unpredictability of precipitation, rising sea levels that contaminate coastal freshwater reserves, and increasing the risk of catastrophic flooding requiring urgent measures (Lovvorn, 2017). Harrington et al. (2016) showed that poor countries will have to face the consequences of climate change such as more frequent heat extremes, whereas the wealthiest countries that are responsible for the major part of CO₂ emissions will be able to cope with the impacts more easily. A recent study (Mazdiyasni et al., 2017) shows that between 1960 and 2009 mean temperatures in India rose more than 0.5°C and this lead to a 146% increase in the heat-related mortality probability events. Most unfortunately, comprehensive agreements on CO₂ reduction have not been reached by the international community. The repeated fiascos of the so-called Conference of Parties (COPs) in Warsaw (CP-19 in 2013), in Lima (COP-20) in 2014, in Paris (COP-21) in 2015, and most recently in Marrakech (COP-22) in November of 2016 to agree on important

reductions on greenhouse gas emissions only worsened the climate change scenario. The major problem being the fact that the major emission emitters China, US, and India does not accept severe cuts. It is true that CO₂ emissions in China increased rapidly from 3299 million tons in 2000 to 9023 million tons in 2013 and that China's share of the world's total CO₂ emissions increased from 14.15% in 2000 to 28.03% in 2013 (IEA, 2015). And if the position of China and India is understandable from an economic view and that of the US is not, it is not only because US is a well-developed economy but above all because on a per capita historical basis the US is 10 times more accountable than China and 25 times more accountable than India for the increase of atmospheric CO₂ above its preindustrial level. Also, statistics on the countries' own emissions only concern emissions that took place within their own border and forget that a great part of those emissions in China is due to production of products consumed by Western countries. This issue is not taken under consideration on the COPs (Peters et al., 2016). Not to mention that different countries have different forest capacities to offset CO₂ emissions. Since the mid 1970s, forest expansion and regrowth in China has lead to a significant carbon storage of 450 million tons (Fang et al., 2001). Worldwide forest sink is responsible for carbon storage of 2400 million tons per year (Pan et al., 2011). Recent studies show that China forest will be able to store 340 million tons per year, thus being able to offset between 6% and 8% of China's future emissions (He et al., 2016). Currently, there are generally two types of market-based instruments to try to reduce CO₂ emissions: one is the emission trading policy based on the amount of pollution control, namely, the carbon trading market; the other is through the tax system or, namely, the carbon tax. The international debate regarding the carbon tax originated in the 1990s when the countries of European community made a commitment to reduce CO₂ emissions (Zhang et al., 2016). A number of authors, particularly those who have applied approaches involving cost-benefit techniques, have all labeled carbon tax as more efficient (Wesseh et al., 2017; Zhang et al., 2017). However, so far it had little success. The EU approved a carbon tax but it has never been implemented (Zhang et al., 2016). Australia repealed its carbon tax in 2014, which was introduced in 2013 because of political and social pressures. In a parallel manner, in the US, despite the fact that the House of Representatives passed a cap-and-trade bill in 2010, nonetheless, Senate did not approve of it (Ramlall, 2017). Therefore it is not foreseeable that in the near future those market-based instruments could have an impact on reducing CO₂ emissions. Even if all the greenhouse gas emissions suddenly ceased, the inertia associated to climatic systems would mean that the rise in the sea level, ocean acidification, and extreme atmospheric events will continue at least in the next 100 years (Clayton, 2001).

In a recent study, researchers at the universities of Sussex, Manchester, and Oxford (Geels et al., 2017) stated that humanity must move faster towards a low-carbon world and that changes in electricity, heat, buildings, industry, and transport are needed rapidly and must happen all together, in order to limit global warming to 2°C this century. Targets for limiting global warming thus should aim to avoid leaving global temperature at Eemian or higher levels for centuries. Such targets now require "negative emissions", i.e., extraction of CO₂ from the air (Hansen et al., 2017). Parker and Geden (2016) also state that if the world wants to stay below 1.5°C of warming it must deploy CO₂ removal on an enormous scale. That is why carbon sequestration constitutes one of

the Grande Challenges of Engineering (Mote et al., 2016). Amoureux et al. (2014) already have suggested that CO₂ should be seen as a commodity that could serve as basis for a new economic industry. Currently this carbon sequestration is carried out mostly through geologic CO₂ storage in saline aquifers (Zhang and Huisingsh, 2017). However, it constitutes a passive strategy that has large risks and also has a very high cost. Carbon capture and storage from the stream of concentrated CO₂ at fossil fuel burning sites such as power plants or steel plants is more efficient and thus less expensive than direct air capture (Hansen et al., 2017). In 2009, Germany initiated, as one of the first nations in the world, a major research program on CO₂ capture and utilization and between 2010 and 2016, approximately 100 million Euros were granted for 33 collaborative research and development projects, consisting of more than 150 individual projects (Mennicken et al., 2016). The flagship program EnCO₂re (2017), one of the five Climate-KICs that started in 2014 with public launch in 2016, currently looks to develop new technologies offering novel ways to use CO₂, increase awareness for CO₂ reuse, and ensure sustainability and social acceptance of materials and products by integrated socio-ecological research. This program is led by Covestro AG (formerly Bayer MaterialScience AG) working with other Climate-KIC companies and university/research partners from several countries including Denmark, Sweden, UK, France, and The Netherlands. Recently, Zimmermann et al. (2017) presented a report on CO₂ utilization status. A McKinsey & Company report estimates that carbon products, especially in concrete, plastics, fuel, and carbon fiber, could be a market worth between 800 billion and 1.1 trillion US dollars by 2030 (Global CO₂, 2016). XPRIZE Foundation, designed to accelerate new technologies by converting CO₂ emissions from industrial facilities into valuable and usable products has created the 20 million US dollar NRG COSIA Carbon XPRIZE. The competition is structured as a two-track prize, with the new technologies tested at either a coal power plant or a natural gas power plant (Cosia, 2017).

It is also worth mentioning the case of the startup “Carbon8 Aggregates,” whose technology combines CO₂ with waste residues from municipal incinerators and energy plants to form calcium carbonate (Carbon8, 2017). Therefore the development of cementitious construction materials based on CO₂ storage will have major eco-efficient as well as economic benefits not only for the construction industry but also for the world’s future. If no other reason would exist it will suffice the fact that it may increase students’ awareness about the importance of carbon sequestration, thus helping to reduce the number of civil engineering students who currently do not believe our actions are causing climate change (Shealy et al., 2016). Books already published on CO₂ storage are mostly concerned on geologic aspects and even those few related to industrial valorization have nothing related to the construction industry.

1.2 Outline of the book

This book provides an updated state of the art on the development of cementitious construction materials based on CO₂ storage. The first part encompasses sequestration methods (Chapters 2–6). In Chapter 2 the importance, advantage, and challenges of

using fly ash as a feedstock for CO₂ mineralization are introduced. The physico-chemical properties of fly ash and their effect on carbonation performance as well as the property changes after carbonation are summarized. Recent progress on the performance of direct aqueous carbonation is also evaluated from both chemistry and kinetic point of views. Moreover, several intensification methods such as operating parameter optimization, additives, reactor development, and wastewater-enhanced carbonation are reviewed. Chapter 3 discusses aqueous-based CO₂ sequestration. The chemistry, processing conditions, engineering aspects, environmental impact, and life cycle of the aqueous-based mineral CO₂ sequestration method are discussed in order to enable the process to be implemented.

Chapter 4 covers the reaction mechanism of direct aqueous carbonation of steel slag. The merits and shortcomings of different steel slag carbonation models are discussed.

The mechanism and benefits of accelerated carbonation curing, the factors affecting the performance of accelerated carbonation curing, and the test methods used by the researchers for evaluating the performance of concrete subjected to accelerated carbonation curing are outlined in Chapter 5. Set-ups for conducting accelerated carbonation curing of concrete are described. Some case studies related to the acceleration carbonation curing of different types of concrete such as normal concrete and self-compacting concrete are included.

Chapter 6 provides a review of five methods for the assessment of CO₂ uptake by cementitious materials, including determination of mass change, *gamma densitometry*, ignition testing method, quantitative X-ray diffraction, and coulometric titration. Limitations and advantages are highlighted.

Carbonation mechanisms are the subject of Part II (Chapters 7–11).

Chapter 7 discusses the microstructural changes in alkali-activated slag mortars after carbonation and reviews factors influencing carbonation in alkali-activated systems, including precursors, activators, CO₂ concentration, and relative humidity. The compressive strength, main reaction products, porosity, and pore structure of alkali activation-based binders before and after carbonation are investigated.

Chapter 8 deals with the reaction mechanisms and associated strength and microstructural development of reactive magnesia cement systems. It reviews the production, characterization, properties, and applications of the main binder phase, MgO, that control the performance of reactive magnesia cement samples. This chapter also discusses the influence of key factors such as binder properties, mix design, curing conditions, and presence of additives on the hydration and carbonation reactions. Current state of the art and gaps in existing literature are highlighted, supported by recommendations to turn limitations into potential advantages.

In Chapter 9 the formation process, physico-chemical properties, carbonation mechanism, carbonation rate, and heavy metal leaching of steel slag and in particular the microstructure, performance, and application of carbonated steel slag as construction materials are discussed.

Chapter 10 discloses results of an investigation concerning the CO₂ sequestration on phosphogypsum from the fertilizers industry, soda solutions, and liquid alkaline wastes from aluminum industries.

Chapter 11 presents CO₂ sequestration on biocement composites. The role of microbes and their enzymes involved in CO₂ sequestration, microbial routes in CaCO₃ formation, biocementation, and the effectiveness of microbially induced calcium carbonate precipitation (MICP) in improving durability of building materials are discussed. Recommendations to employ the MICP technology at commercial scale and reduction in cost of application are provided in this review.

Finally, part III presents several case studies (Chapters 12–18).

In Chapter 12 active carbonation techniques adopted for crushed concrete aggregate derived from the Construction and demolition waste and the resulting properties of the CO₂ cured recycled concrete aggregate are discussed. In addition, the mechanical properties, durability properties, and microstructure of CO₂-cured recycled aggregate concrete are also reviewed.

Chapter 13 concerns a case study related to CO₂ sequestration on fly ash/waste glass alkaline-based mortars with recycled aggregates. Compressive strength, hydration products, carbon footprint, and cost analysis are studied in it.

Chapter 14 discloses results of an investigation concerning CO₂ sequestration on fly ash/waste glass alkaline-based mortars and different sodium hydroxide concentrations. Properties, durability, carbon footprint, and cost analysis are studied in.

Chapter 15 addresses the case of fly ash/waste glass alkaline-based mortars with recycled aggregates reinforced by hemp fibers exposed to accelerated CO₂ curing. Compressive strength, flexural strength, and numerical simulations with a finite element method are studied in it.

Chapter 16 presents results of an investigation concerning the performance of fly ash/waste glass alkaline-based mortars with recycled aggregates reinforced by hemp fibers exposed to accelerated CO₂ curing. Properties, freeze-thaw resistance, and carbon footprint are studied in this chapter.

Chapter 17 gives an overview of CO₂ sequestration on concrete masonry blocks.

A wide variety of factors influencing the accelerated carbonation process are discussed. Also, the kinetic model, dimensional stability, and microstructure of concrete blocks after accelerated carbonation are described.

Chapter 18 closes Part III with a chapter on the production of cement-bonded particleboards, discusses the current limitations of particleboards in production and application, articulates the roles of CO₂ curing in particleboard manufacture, evaluates different CO₂ curing techniques, illustrates mechanisms of CO₂ curing, characterizes major controlling factors, and suggests future directions of particleboard production via CO₂ utilization.

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